



# FOOTPRINT

(A Screening Model for Estimating the Area of a Plume Produced from Gasoline Containing Ethanol)

## ***Version 1.0***

*A. Noman M. Ahsanuzzaman, Ph. D.<sup>1</sup>*

*John T. Wilson, Ph. D.<sup>2</sup>*

*Mingyu Wang, Ph. D.<sup>1</sup>, and Robert C. Earle<sup>1</sup>*

<sup>1</sup>Shaw Environmental & Infrastructure Inc.

<sup>2</sup> U.S. EPA, Office of Research and Development, National Risk Management Research Laboratory

### **EPA Project Officer**

*Mary S. McNeil*

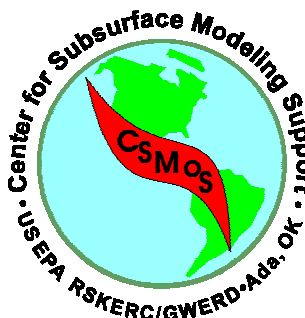
U.S. EPA, Office of Research and Development, National Risk Management Research Laboratory

***Center for Subsurface Modeling and Support***

***Ground Water and Ecosystem Restoration Division***

***Ada, OK***

***U.S. Environmental Protection Agency***



## **NOTICE**

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# Overview

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## Purpose

Many grades of gasoline contain both ethanol and petroleum hydrocarbons such as benzene and the other BTEX compounds. Ethanol can inhibit the natural biodegradation of BTEX compounds in ground water (Deeb et al., 2002), causing the plume of BTEX compounds to be larger than they would be if the ethanol were not present in the gasoline. FOOTPRINT is a simple and user-friendly screening model that can be used to estimate the effect of ethanol in gasoline on the surface area of the plume of benzene or any of the other BTEX compounds in groundwater. FOOTPRINT estimates the overall surface area of a plume that is contained within two biodegradation zones, one zone where ethanol is present and there is no biodegradation of BTEX compounds, surrounded by a second zone where the ethanol has been removed by natural biodegradation and the BTEX compounds are biologically degraded. In the second zone, the rate constant for biodegradation of the BTEX compound does not change as water moves along the flow path.

The software uses a modified version of the Domenico (1987) model that was published by Martin-Hayden and Robbins (1997). The model of Martin-Hayden and Robbins (1997) is an approximate analytical solution of the advective-dispersive solute transport equation with first-order decay. Natural degradation of ethanol at concentrations expected from a gasoline spill is likely to be a zero-order process. The Domenico model as used in FOOTPRINT is further modified to allow the option of zero-order decay for either ethanol or the BTEX compounds (see Appendix B for details). FOOTPRINT can be used to estimate the surface area of the plume or the concentration at any given point down-gradient from the source. It can also be used to estimate the behavior of any chemical of concern (COC) in the absence of ethanol.

# Software Installation

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## How to Install?

To install the software, run '**FOOTPRINTsetup.exe**'. The software will guide the user through the installation process.

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## Software Requirements

**Microsoft Excel** software must be installed on the computer. FOOTPRINT displays the model outputs in Excel Chart format.

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## Disclaimer of Liability

With respect to FOOTPRINT software and associated documentation, neither the United States Government nor any of their employees, assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed. Furthermore, software and documentation are supplied "as-is" without guarantee or warranty, expressed or implied, including without limitation, any warranty of merchantability or fitness for a specific purpose.

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## Disclaimer of Endorsement

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# Theory

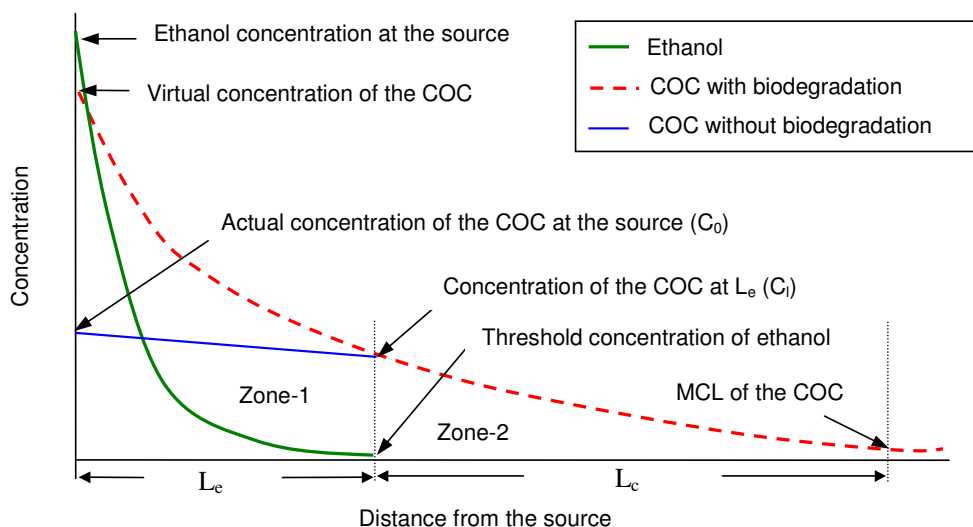
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## Conceptual Model

The conceptual model used in FOOTPRINT is an extension of the model proposed by Deeb et al. (2002). Figure 1 shows the conceptual model used in FOOTPRINT. The following are the assumptions in the FOOTPRINT conceptual model.

1. The release of gasoline containing ethanol and BTEX compounds is located at the water table (or at the top of the aquifer).
2. Ethanol dissolves in ground water and disperses as the ground water moves away from the release of gasoline. The rate constant for biodegradation of ethanol does not change as water moves along the flow path.
3. Biodegradation of the BTEX compounds in ground water is negligible until the concentration of ethanol drops to a threshold concentration. The threshold concentration is an input to FOOTPRINT. Following Deeb et al. (2002), the default value of the threshold is 3 mg/L. When concentrations of ethanol are above the threshold, the only processes that reduce the concentration of BTEX compounds are dispersion and sorption.
4. Biodegradation of the BTEX compound that is addressed in a particular model run is only allowed when the concentration of ethanol is below the threshold concentration. Biodegradation of the BTEX compound begins along a flow path in the aquifer when the concentration of ethanol falls below the threshold. The rate constant for biodegradation of the BTEX compound does not change as water moves further along the flow path.
5. FOOTPRINT estimates plume length at the water surface of the aquifer and it assumes an infinite depth for the aquifer.

**Figure 1: Conceptual Model of FOOTPRINT**



A three-dimensional solute transport model developed originally by Domenico (1987) and later modified by Martin-Hayden and Robbins (1997) is used to estimate the plume area. The modified Domenico model of Martin-Hayden and Robbins (1997) considers one-dimensional flow, three-dimensional dispersion, and first-order biodegradation. In addition, the model assumes a two-dimensional source zone perpendicular to ground water flow with a constant and continuous concentration of contaminant leaving the source, and an initial concentration of contaminant down gradient from the source of zero. The modified Domenico model of Martin-Hayden and Robbins (1997) is inadequate to describe the effect of ethanol on BTEX biodegradation because it only considers one biodegradation rate, while the conceptual model for FOOTPRINT requires no biodegradation of BTEX near the source where the concentration of ethanol is above the threshold. The conceptual model in FOOTPRINT is designed to use the modified Domenico model to overcome this limitation.

The FOOTPRINT model was developed for the BTEX compounds in gasoline, but the model is appropriate for any chemical of concern (COC) where biodegradation is inhibited by the presence of ethanol. FOOTPRINT can also be calibrated to describe the behavior of any COC, without the influence of ethanol.

## Simulation Steps

Following are the steps used in FOOTPRINT to estimate the plume area based on the conceptual model shown in Figure 1.

1. Run the modified Domenico model for ethanol at steady-state (or, transient) conditions to estimate the distance  $L_e$  (see Figure 1), which is the distance from the source to where the ethanol concentration drops below the threshold concentration of ethanol.



2. Run the modified Domenico model for the chemical of concern (COC) with no biodegradation to get the concentration at  $L_e$  ( $C_l$ ).
3. Simulate the inverse solution to the modified Domenico model to determine a virtual concentration of the COC ( $C_v$ ) that would be expected at the source for  $C_l$ , assuming that the COC was biodegrading at a given rate from the source to  $L_e$ , i.e., Zone-1 (see Figure 1).
4. Run the modified Domenico model for the virtual concentration of the COC at the source ( $C_v$ ) to get the distance  $L_c$  (i.e., Zone-2), where the steady-state (or transient) concentration of the COC drops to the MCL (maximum contaminant level) or any target ground water concentration.
5. Calculate the area of the plume. In order to calculate the area, the model domain is divided into a finite number of cells. Concentrations of the COC are calculated at every cell in the model domain. The number of cells that exceed the MCL (or the target concentration) in both zones ( $L_e$  and  $L_c$ ) are counted and used to estimate the plume area.

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## Potential Limitations of FOOTPRINT

FOOTPRINT uses a modified version (Martin-Hayden and Robbins, 1997) of the Domenico model (1987). Potential limitations of fate and transport models based on the Domenico analytical solutions have been identified in recent journal articles (Guyonnet and Neville, 2004; Srinivasan et al., 2007; and West et al., 2007). CSMoS (Center for Subsurface Modeling Support) acknowledges that fate and transport models based on the Domenico analytical solutions are approximate solutions of the advective-dispersive solute transport equation; therefore they could generate error for a given set of input parameters when compared with the exact solutions to the advective-dispersive solute transport equation as provided by Wexler (1992).

In steady state simulations, the approximation error is most sensitive to high values of longitudinal dispersivity (Srinivasan et al., 2007; and West et al., 2007). West et al. (2007) conducted a sensitivity analysis and reported in Figure 2 of that article that the approximation error is 16% when longitudinal dispersivity is 10% of the plume length. Approximation errors in FOOTPRINT may be significant at values of longitudinal dispersivity greater than 10% of the plume length. In real-world modeling applications, longitudinal dispersivity is most often a calibration parameter, not a parameter that is measured in the field. If longitudinal dispersivity is varied to calibrate FOOTPRINT to a particular plume, use values of longitudinal dispersivity that are less than 10% of the plume length to minimize the approximation error.

In transient simulations, in addition to the approximation error that is associated with large values of dispersivity, there is also approximation error associated with early values of simulation time. The early values of simulation time where approximation error is a possibility can be identified by comparing increasing values of simulation time until the predictions of plume behavior stabilize.

# Input

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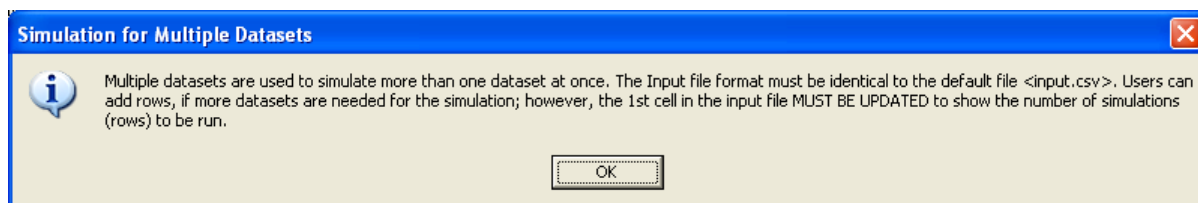
## Input Options

### Single Dataset

This option uses a single set of data as input. The input data are entered from the screen. The user can change any data in the input screen and run the model.

### Multiple Datasets

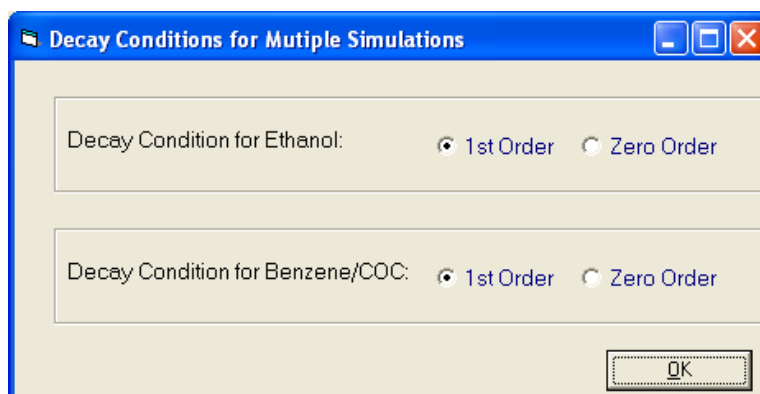
This option determines plume area for more than one dataset. The data are input from a 'comma delimited' text file (\*.csv). The user can create a new input file with multiple sets of data and get the output quickly. Under this option, the only input from the screen is the approximate domain length. Please see the **Input File Format** for details. The following pop-up screen will appear once the 'Multiple Datasets' option is selected.



### Input File Format

*The 'input.csv' file can be found in the same directory where the software is installed.*

The Input File is in 'comma delimited' (\*.csv) format. An example of the required format for the Input File is provided in the file titled input.csv. The example file is stored in the same directory where FOOTPRINT was installed. **Double-Click** the icon above the 'Open' label next to the 'Browse' button in FOOTPRINT to view and modify the example file in MS Excel. After modifications are made, save the file under a new name as \*.csv. ***The first cell in the modified Input File should represent the number of rows or datasets in the Input File.*** The other data fields are explained by their column headings. The decay rates (first or zero order) for ethanol and the COC should be input in respective cells. The user will be asked to define the decay rate law (first or zero order) of both the COC and ethanol from a pop-up screen (see below) as soon as the 'Multiple Datasets' option is selected.



The user must input the grid spacing in the longitudinal direction to ground water flow (called, column spacing) and in the transverse direction (called, row spacing) for each simulation. This is important to speed up the simulation. For smaller values of the biodegradation rate, the domain size can become very large, and the simulation time will increase. To reduce the simulation time in such cases, increase the column and row spacing. *To minimize run time, run a single dataset case for the slowest biodegradation rate to obtain the smallest usable value for **approximate domain length**, and then use that length in the multiple datasets option.* Otherwise, the simulation might terminate before completion. Note that input of an excessively large approximate domain length will not increase the simulation time, as FOOTPRINT optimizes the domain length during the simulation.

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## Advection

*Where the velocity is shown in 'blue color'.*

Calculate the groundwater seepage velocity from the input of hydraulic conductivity, hydraulic gradient, and effective porosity. To calculate the velocity, press the 'Calculate' button. You can also directly input the velocity by changing the value in the velocity input box. The model uses the value shown in the velocity input box. Note that clicking the 'Calculate' button will overwrite the manually entered value.

---

## Dispersion

Longitudinal, transverse, and vertical dispersivity are input in this section. In the absence of a value for longitudinal dispersivity ( $\alpha_x$ ) that is extracted from site specific field data, there are two common approaches to estimate a value that can be used to calibrate a transport and fate model.

Following Pickens and Grisak (1981):

$$\alpha_x = 10\% L$$

where L is the longitudinal distance to the reference point from the source of the chemical of concern.

Following Xu and Eckstein (1995):

$$\alpha_x = 3.28 * 0.83 * [\log_{10} (L/3.28)]^{2.414}$$

where L is the length of the plume **in feet**.

It is a common practice to calibrate groundwater flow models with a value of transverse dispersivity that is 10% of longitudinal dispersivity.

By choosing a very small vertical dispersivity (the default value), the user can limit the model to two-dimensional dispersion. Note that FOOTPRINT estimates the effect of ethanol on the plume length of the BTEX compound or COC **at the water surface** of the aquifer.

FOOTPRINT assumes an infinite depth for the aquifer. When the COC [No Ethanol] Run Option is selected, and a value is assigned to Z such that the observation point is specified to be below the source thickness, be aware that the predicted concentration may be very low, giving the impression that the plume has not reached that far in the longitudinal direction, when in actuality, the plume may be above the observation point.

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## General Inputs

It is good practice to conduct a sensitivity analysis of plume length and area for the model outputs over the range of expected values of the calibration parameters.

### Source Thickness

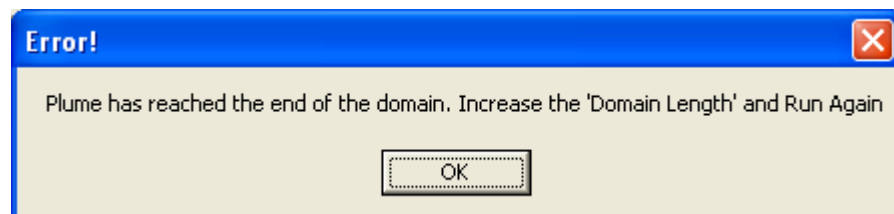
This is the dimension of the source along the vertical direction in the aquifer. FOOTPRINT assumes an infinite aquifer dimension in the vertical direction.

### Source Width

This is the dimension of the source along the transverse (lateral) direction, perpendicular to the direction of ground water flow.

### Approximate Domain Length

This is the domain length along the direction of ground water flow. The user is required to input **a large value** in this field. FOOTPRINT itself optimizes the longitudinal domain length. This input is required to start the simulation. If the user inputs a value that is too small, a message box will pop-up (see below), asking them to increase the input value. This input is also used to scale the longitudinal dimension of the concentration vs. distance output (see the output section).



*Longitudinal spacing is the grid spacing along the direction of flow.*

*Transverse spacing is the grid spacing along the direction perpendicular to flow.*

## Grid Spacing

Concentration is calculated at the center of each grid cell. Therefore, smaller grid spacing will provide better accuracy in estimating the plume area. However, smaller grid spacing will require more computation time.

The user is required to input the grid spacing along the longitudinal and transverse directions to the ground water flow.

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## Ethanol/Oxygenate Alcohol Source

### Ethanol Concentration at Source

This is the concentration in ground water at the source of the plume of ethanol or another alcohol used as an oxygenate such as methanol, or of biofuels, such as, butanol or propanol.

### Biodegradation Rate

The user has the choice to assume either a first order or zero order rate constant in the model run. This is the rate of biodegradation in the aqueous phase. **If the user assumes that the chemical is decaying at a constant rate in both the aqueous and adsorbed phases, you need to multiply the decay constant in the aqueous phase by the retardation factor.**

If the user wants to use different decay rates for the aqueous phase and sorbed phase, you can input a lumped decay rate. Appendix C provides equations to estimate the lumped decay rate for zero order rates and appendix D provides equations for first order rates (see Equation 5 in both appendices C and D for detail).

To facilitate a sensitivity analysis for rates of biodegradation of ethanol in ground water, a synopsis of rates of ethanol biodegradation available from the literature are provided in Table 1 (see page 22).

### Threshold Ethanol Concentration

This is the concentration of ethanol below which biodegradation of the COC is allowed in FOOTPRINT. The default value is 3 mg/L (Deeb et al., 2002).

### Retardation Factor

This is the retardation factor for ethanol or other alcohol (R). In most aquifer sediment, R for ethanol is near 1.0.

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## Benzene or Other Chemical of Concern (COC)

The chemical of concern (COC) is the chemical for which the simulation is conducted. COC could be any of the BTEX compounds. The output represents the simulation for the COC.

### Concentration at Source

This is the actual concentration of the COC in ground water at the source. The user has the option to assume either a constant concentration at the source or a source concentration that decays exponentially with time. The original Domenico model assumes a constant concentration at the source. If the source is decaying over time, the user can estimate a first-order decay constant for the source concentration by fitting an exponential decay model to the long term monitoring data for concentrations of the COC at the source (see Aziz et al., 2002, BIOCHLOR Version 2.2 manual for detail). Note that the decaying source is only applicable for the COC.

### Biodegradation Rate

The user has the choice to assume either a first order or zero order rate constant in the model run. This is the rate of biodegradation in the aqueous phase. **If you assume that the chemical is decaying at a constant rate in both the aqueous and adsorbed phases, you need to multiply the decay constant in the aqueous phase by the retardation factor.** If you want to use different decay rates for the aqueous phase and sorbed phase, you can input a lumped decay rate. Appendix C provides equations to estimate the lumped decay rate for zero order rates and appendix D provides equations for first order rates (see Equation 5 in both appendices C and D for detail).

To facilitate a sensitivity analysis for rates of biodegradation of the BTEX compound or other COC in ground water, a synopsis of rates of biodegradation available from the literature are provided in Tables 2, 3, 4, and 5 (see pages 23-24).

### Maximum Contaminant Level (MCL)

This is the concentration below which concentrations of the COC are considered acceptable. The plume area from the simulation sums the areas of the cells in the grid where the concentration of the COC is above this value.

### Source Decay Rate

This is the decay rate for the COC at the source. If the COC concentration is decreasing at the source with time, the user can use this option by selecting the 'Decaying Source' box. Appendices A and B provide the modified Domenico model for decaying source where the plume is decaying at first and zero order, respectively. The mathematics imposes an upper limit on the rate of source decay, depending on other input data. The **upper limit of the source decay rate** for the first and zero order models are provided in the appendices (see Equation 7 in Appendix A and Equation 14 in Appendix B). FOOTPRINT uses an additional 20% factor of safety on the

limiting values obtained from these equations in order to ensure that the model will run properly.

In addition to the limiting conditions in the modified Domenico model for decaying source, **FOOTPRINT imposes a further constraint on the source decay rate**. The model does not allow the COC concentration to drop below the target concentration or the MCL inside Zone-1, where the ethanol concentration is higher than the threshold limit. FOOTPRINT estimates the limiting value of the source decay rate (see Figure 2). It simulates the inverse model to estimate a virtual concentration of COC at the source for 10% more than the MCL (or target concentration) at  $L_c$ .

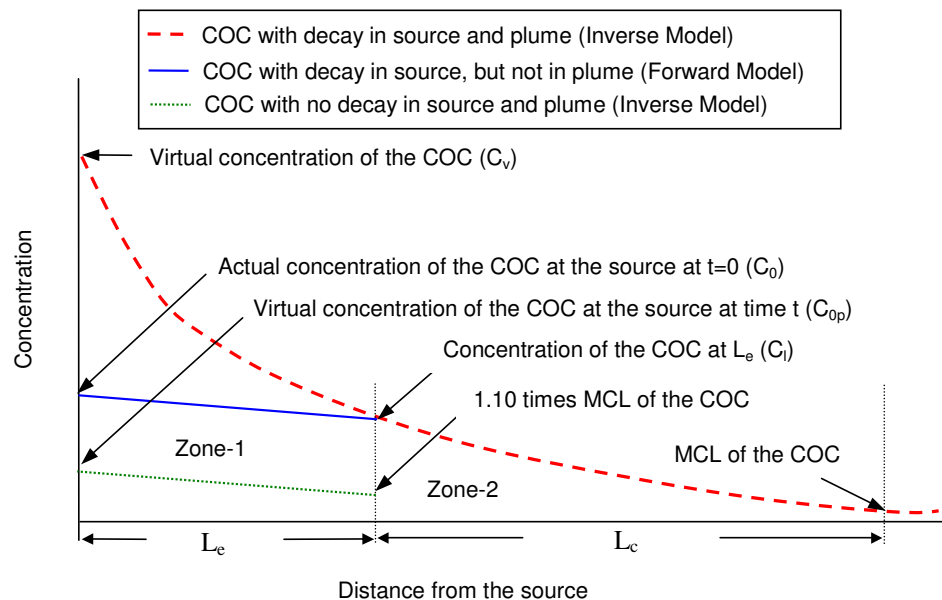
The following equation provides the limiting value of first-order source decay rate used in FOOTPRINT (note that an additional 10% factor of safety is assumed).

$$K_s \leq 0.9 \times \frac{1}{t} \ln \left( \frac{C_0}{C_{0p}} \right) \quad (1)$$

where,  $K_s$  is the decay rate of COC at the source (1/yr),  $t$  is the simulation time in years,  $C_0$  is the initial concentration of COC at the source, and  $C_{0p}$  is the virtual concentration of the COC necessary to produce a concentration of the COC at the end of zone-1 ( $L_c$ ) that is equal to 1.1 times the MCL, when there is no decay or degradation of the COC in the source and the plume.

Typical values for the rate of decay of concentrations of benzene and xylene in ground water in the LNAPL source area of gasoline spill sites are 0.135 and 0.073 per year respectively for sites that have not been remediated and 0.80 and 1.1 per year respectively for sites where some source remediation has been attempted (Peargin, 2000).

**Figure 2: Technique to Estimate the Limiting Source Decay Rate**



## Retardation Factor

This is the retardation factor ( $R$ ) for the individual BTEX compound or COC.  $R$  is a function of the partitioning coefficient of the compound between soil organic matter and water ( $K_{oc}$ ), the organic matter content of the soil ( $f_{oc}$ ), the soil bulk density ( $p_b$ ), and the soil porosity ( $n$ ).

$$R = 1 + \frac{p_b}{n} K_p \quad (2)$$

The unit for  $p_b$  is typically Kg/L,  $n$  is dimensionless, and the unit for  $K_p$  is L/Kg.  $K_p$  is usually estimated as the product of  $K_{oc}$  (L/Kg) and  $f_{oc}$  (Kg/Kg).

Typical value for  $p_b$  ranges from 1.37 to 1.81 Kg/L for fine to coarse sand, and from 1.36 to 2.19 Kg/L for fine to coarse gravel (Domenico and Schwartz, 1990). Typical value for  $n$  ranges from 0.1 to 0.35 for sand, 0.1 to 0.25 for gravel, and from 0.01 to 0.3 for silt (Domenico and Schwartz, 1990). Note that  $p_b$  and  $n$  are correlated through the following equation.

$$p_b = SG (1 - n) p_w \quad (3)$$

where,  $SG$  = soil specific gravity (typically range from 2.65 to 2.70), and  $p_w$  = density of water (typically, 1 Kg/L).

Typical values for  $K_{oc}$  for benzene, toluene, ethylbenzene, and the xylenes are 38, 95, 135, and 240 L/Kg respectively (ASTM, 2002). Typical values for  $f_{oc}$  range from 0.0002 to 0.2. When site-specific data are not available, use a default value of 0.001 for  $f_{oc}$  (ASTM, 2002). The corresponding value of  $R$  is 1.2 for benzene, 1.6 for toluene, 1.8 for ethylbenzene, and 2.4 for the xylenes.



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## Run Options

Click the 'Run' button to execute the model.

### Steady State

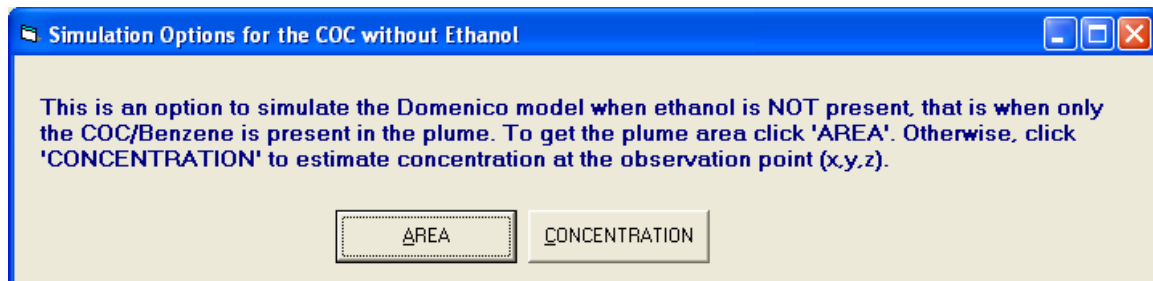
This option runs the model under steady-state conditions. The model uses a simulation time equal to 100 years to ensure a steady state condition. If you want to run the model for any other time interval, change the value of 'Simulation Time' in the Run Options input box.

### Transient

This option runs the model under transient conditions. If this option is selected, you are required to input the time interval (years) you desire in the 'Simulation Time' input box.

### COC Only [No Ethanol]

This option runs the simulation for the COC without the presence of ethanol. There is one decay zone for the COC instead of two. Once the 'COC Only [No Ethanol]' option is checked, the following message will pop-up on the screen.



To obtain the plume area click on the 'AREA' button, otherwise click the 'CONCENTRATION' button to obtain the concentration at any given observation point in the aquifer. Input the coordinates of the observation point, and then click the 'Run' button to view the concentration in a pop-up window. This option can be run under either steady-state or transient conditions.

The 'COC Only [No Ethanol]' option can be run for both single and multiple dataset options. Under the single dataset option, when the 'AREA' button is clicked, the simulation will use the input data from the screen for the COC to estimate the plume area. Under the multiple datasets option, the 'AREA' button will use the input file for the multiple datasets option to estimate the plume areas. The 'CONCENTRATION' button is inactive under the 'COC Only' option for multiple datasets run.

# Output

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## Numeric

This option shows the numeric output from FOOTPRINT.

### Single Dataset

This option shows the output for the 'single dataset' run from the screen. The outputs shown are the area of the plume along with four other values ( $L_e$ ,  $L_e+L_c$ ,  $C_l$ ,  $C_v$ ) from the conceptual model. The figure depicting the conceptual model is also shown in the window. The user can print the output window by clicking the 'Print' button.

### Multiple Datasets

This option shows the outputs for the multiple datasets simulation. The outputs shown are simulation name, plume area in square feet, and plume area in acres. The user can open the output file (*OutMult.xls*) in MS Excel by 'double clicking' on the window.

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## Graphic

This option shows the graphical output from FOOTPRINT.

### Plume

This option provides a figure that shows the plume in an aerial view. The figure shows the distribution of concentrations of the COC that are above the target concentration (MCL). This option can only be viewed for the single dataset option. *Note that the grid spacing used in the figure is different from that used in determining plume area.*

The color in the middle portion of the figure represents the area where the concentration of the COC exceeds the target concentration. The other color along the boundary of the plume represents the area where the concentration of the COC is less than the target level (MCL). The figure was created using the **surface** option for 'chart type' in Excel. The user can view the figure in MS Excel by 'double clicking' on the figure (*OutArea-1.xls*). By double clicking the upper margin of the grid (within Excel), you select the chart and can modify the chart using options from the "Chart" drop down menu in Excel. You can also view the output data by selecting the "sheet1" tab of the spreadsheet in Excel. Any data in the "sheet1" tab is the target concentration (MCL), not the actual computed concentration for that cell.

FOOTPRINT records only the target concentration (MCL) for all cells exceeding that value.

## Conc. vs. Distance

This option shows the concentration vs. distance along the centerline of the plume. This option is only available for the single dataset input option. You can also view the figure for the 'COC Only [No Ethanol]' option by checking that box and then selecting the menu option 'Conc. vs. Distance' under the 'Graphic' option from the 'Output' options (Output\Graphic\Conc. vs. Distance). By 'double clicking' on the figure, the user can open the output file (*CvsX-1.xls*) in Excel.

# Additional Menu Options

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## Print Screen

This option prints the input screen window.

---

## Exit

This option will close FOOTPRINT.

---

## Help

### Help Topics

This option opens the help file. The help file is created from this user's manual.

### About

This option identifies the software developers and provides a disclaimer.

# Tutorials

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## Single Dataset

### Steady State

To run FOOTPRINT for the default values, select the 'Single Dataset' and the '**Steady-State**' input options, then click the 'Run' button. FOOTPRINT will run for the input values in the screen. To view the output, select the desired options from the Output menu.

### Transient

To run FOOTPRINT for the default values, select the 'Single Dataset' and the '**Transient**' input options, then click the 'Run' button. The model will run for the input values in the screen, for the particular time selected in the Simulation Time option. To view the output, select the desired options from the output menu.

---

## Multiple Datasets

### Using the Sample Input File

Select the 'Multiple Dataset' and click the 'Run' button. The model will run for the input values in the sample input file 'input.csv'. To view the sample input file, double-click on the icon above the 'Open' label next to the 'Browse' button. To view the output, select the desired options from the output menu.

### Modifying the Sample Input File

To practice modifying the input file and run the model, do the following:

1. Open the sample input file (input.csv) by double-clicking on the icon above the 'Open' label next to the 'Browse' button.
2. Add two rows of data and change the first cell value to 5.  
*Please note that the first cell in the data file should represent the number of rows/datasets in the input data file.*

3. Save the file as input1.csv (or any other name in \*.csv format). As a default, the saved file is put in the same directory as the FOOTPRINT application. This is usually the 'Program Files' file under the local disk. It may be more convenient to backup your input files, and to transfer files to another computer, if they are saved in a separate directory. Please remember to save the file in \*.csv (comma delimited) format.
4. Exit from MS Excel.
5. Update the 'Input File Name' to input1.csv (or whatever name you selected for the modified file). You must input the entire path of the file correctly. Alternatively, you can click the Browse button and navigate through your directories to find the input file in the directory where you saved it, and then press the 'open' button to open it into FOOTPRINT.
6. Run the model.
7. To view the output, select the respective menu option.

# Typical Values of Biodegradation Rates for Benzene and Ethanol

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## Biodegradation Rates for Ethanol

FOOTPRINT has the option to run the model using either a first-order or a zero-order rate for biodegradation of ethanol. Since a spill of ethanol-blended gasoline typically results in a very high concentration of ethanol in ground water, the biodegradation process tends to follow zero-order rate law instead of first-order rate law. Table 1 provides some values of zero-order decay rates for ethanol that were extracted from field studies and laboratory studies. Note that the two highest values of decay rates were resulted from continuous injection of ethanol at the source, while ethanol was released as a slug in the other studies.

Table 1. Zero-order decay rates for ethanol.

| Study Type                                | Redox Process     | Decay Rate |         | Reference                   |
|---|-------------------|------------|---------|-----------------------------|
|   |                   | mg/L/day   | mg/L/yr |                             |
| Field                                     | Methanogenesis    | 55         | 20075   | Buscheck et al. (2001)      |
| Field                                     |                   | 2.3        | 839.5   | Corseuil et al. (2000)      |
| Field                                     |                   | 9          | 3285    | Mravik et al. (2003)        |
| Field                                     |                   | 14         | 5110    | Zhang et al. (2006)         |
| Field                                     |                   | 18         | 6570    | Mocanu et al. (2006)        |
| Field                                     |                   | 1.4        | 511     | Mocanu et al. (2006)        |
| Field, Continuous Ethanol Injection       | Methanogenesis    | 500        | 182500  | Mackay et al. (2006)        |
| Lab                                       | Sulfate Reduction | 8          | 2920    | Corseuil et al. (1998)      |
| Lab                                       | Methanogenesis    | 14         | 5110    | Corseuil et al. (1998)      |
| Lab                                       | Methanogenesis    | 34         | 12410   | Suflita and Mormile (1993)  |
| Lab                                       | Iron Reduction    | 11         | 4015    | Corseuil et al. (1998)      |
| Lab, Column, Continuous Ethanol Injection |                   | 13,000     | 4745000 | Da Silva and Alvarez (2002) |

# Biodegradation Rates for Benzene

FOOTPRINT has the option to run the model with either first-order or zero-order rate constants for biodegradation of benzene or any other COC. Table 2 presents the mean, the 90<sup>th</sup>-percentile, and the range of first-order decay rates for BTEX compounds summarized from different field/in-situ studies under anaerobic conditions. Table 3 presents the mean, the median, the 25<sup>th</sup>-percentile, the 75<sup>th</sup> percentile, the 90<sup>th</sup> percentile, and the range for first-order decay rate constants for benzene under different anaerobic conditions. Table 4 provides first-order decay rate constants for benzene at different sites across the United States. Finally, Table 5 provides zero-order decay rate constants for BTEX compounds from field/in-situ studies under anaerobic conditions. Suarez and Rifai (1997) and Aronson and Howard (1997) provide further detail about the decay rates of benzene and the BTEX compounds.

Table 2. First-order decay rate constants for BTEX compounds from field/in-situ studies<sup>ξ</sup>

| Compounds    | Unit    | Mean  | 90th-percentile | Minimum | Maximum | Number of data |
|--------------|---------|-------|-----------------|---------|---------|----------------|
| Benzene      | (1/day) | 0.003 | 0.009           | 0       | 0.023   | 45             |
|              | (1/yr)  | 1.10  | 3.29            | 0       | 8.40    |                |
| Toluene      | (1/day) | 0.24  | 0.27            | 0       | 4.3     | 43             |
|              | (1/yr)  | 87    | 97              | 0       | 1600    |                |
| Ethylbenzene | (1/day) | 0.22  | 0.034           | 0       | 6.0     | 33             |
|              | (1/yr)  | 80    | 12              | 0       | 2200    |                |
| m-Xylene     | (1/day) | 0.031 | 0.066           | 0       | 0.32    | 30             |
|              | (1/yr)  | 11    | 24              | 0       | 116     |                |
| o-Xylene     | (1/day) | 0.019 | 0.042           | 0       | 0.21    | 27             |
|              | (1/yr)  | 7.0   | 15.3            | 0       | 78      |                |
| p-Xylene     | (1/day) | 0.013 | 0.035           | 0       | 0.081   | 25             |
|              | (1/yr)  | 4.8   | 12.8            | 0       | 30      |                |

<sup>ξ</sup> Source: Suarez and Rifai (1997)

Table 3. First-order decay rate constants for benzene at different redox conditions<sup>ξ</sup>

| Redox Process   | Sulfate Reduction |        | Methanogenesis |        | Iron Reduction |        |
|-----------------|-------------------|--------|----------------|--------|----------------|--------|
| Unit            | (1/day)           | (1/yr) | (1/day)        | (1/yr) | (1/day)        | (1/yr) |
| Mean            | 0.008             | 3.0    | 0.01           | 3.7    | 0.009          | 3.3    |
| Median          | 0.003             | 1.10   | 0              | 0      | 0.005          | 1.8    |
| 25th-percentile | 0                 | 0      | 0              | 0      | 0              | 0      |
| 75th-percentile | 0.006             | 2.2    | 0.006          | 2.2    | 0.011          | 4.0    |
| 90th-percentile | 0.023             | 8.4    | 0.033          | 12.1   | 0.024          | 8.8    |
| Minimum         | 0                 | 0      | 0              | 0      | 0              | 0      |
| Maximum         | 0.049             | 17.9   | 0.077          | 28     | 0.034          | 12.4   |
| Number of data  | 16                |        | 15             |        | 20             |        |

<sup>ξ</sup> Source: Suarez and Rifai (1997)



Table 4. First-order decay rate constants for benzene from field studies summarized by Aronson and Howard (1997)

| Site Name                                | Redox Process                                  | Rate Constant |           |
|--|--|---------------|-----------|
|  |  | (1/day)       | (1/yr)    |
| Rocky Point, NC                          | Iron reduction                                 | 0.0002        | 0.073     |
| Tibbett's Road Site, Barrington, NH      | Iron reduction                                 | 0.00011       | 0.040     |
| Tibbett's Road Site, Barrington, NH      | Iron reduction                                 | 0.0022        | 0.80      |
| Bemidji, MN                              | Methanogenesis<br>Iron and Manganese reduction | 0.017         | 6.2       |
| Patrick AFB, FL                          | Methanogenesis                                 | 0.01          | 3.7       |
| Traverse City, MI                        | Methanogenesis                                 | 0.0071        | 2.6       |
| Sleeping Bear Dunes, Natl. Lakeshore, MI | Methanogenesis<br>Nitrate/Sulfate reduction    | 0.00043       | 0.157     |
| Sleeping Bear Dunes, Natl. Lakeshore, MI | Methanogenesis<br>Nitrate/Sulfate reduction    | 0.002-0.004   | 0.73-1.46 |
| Hill AFB, Utah                           | Sulfate reduction                              | 0.0072-0.046  | 2.6-16.8  |
| Hill AFB, Utah                           | Sulfate reduction                              | 0.028         | 10.2      |
| Hill AFB, Utah                           | Sulfate reduction                              | 0.038         | 13.9      |

Table 5. Zero-order anaerobic decay rates for BTEX compounds from field/in-situ studies<sup>ξ</sup>

|                  |            | Mean  | Median | 25th-percentile | 75th-percentile | 90th-percentile | Range      | Number of data |
|------------------|------------|-------|--------|-----------------|-----------------|-----------------|------------|----------------|
| Benzene          | (mg/L/day) | 0     | 0      | 0               | 0               | 0               | 0-0.001    | 5              |
|                  | (mg/L/yr)  | 0     | 0      | 0               | 0               | 0               | 0-0.37     |                |
| Toluene          | (mg/L/day) | 0.15  | 0.09   | 0.007           | 0.108           | 0.37            | 0.007-0.54 | 5              |
|                  | (mg/L/yr)  | 55    | 33     | 2.6             | 39              | 134             | 2.6-197    |                |
| Ethylbenzene     | (mg/L/day) | 0.087 | 0.05   | 0.005           | 0.067           | 0.21            | 0.003-0.31 | 5              |
|                  | (mg/L/yr)  | 32    | 18     | 1.83            | 24              | 78              | 1.1-113    |                |
| <i>m</i> -Xylene | (mg/L/day) | 0.23  | 0.1    | 0.006           | 0.108           | 0.61            | 0.005-0.95 | 5              |
|                  | (mg/L/yr)  | 85    | 37     | 2.2             | 39              | 220             | 1.83-350   |                |
| <i>o</i> -Xylene | (mg/L/day) | 0.127 | 0.007  | 0.002           | 0.007           | 0.38            | 0-0.62     | 5              |
|                  | (mg/L/yr)  | 46    | 2.6    | 0.73            | 2.6             | 136             | 0-230      |                |

<sup>ξ</sup> Source: Suarez and Rifai (1997)

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## Appendix A : Background Theory of FOOTPRINT

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Ahsanuzzaman, A. N. M., and Wilson, J. T., FOOTPRINT: A Computer Application for Estimating Plume Areas of BTEX Compounds in Ground Water Impacted by a Spill of Gasoline Containing Ethanol, *2005 NGWA Conference on MTBE and Perchlorate: Assessment, Remediation, and Public Policy*, National Ground Water Association, San Francisco, CA, 2005.

FOOTPRINT: A Computer Application for Estimating Plume Areas of BTEX Compounds in Ground Water Impacted by a Spill of Gasoline Containing Ethanol

### *Abstract*

Ethanol has a potential negative impact on the natural biodegradation of other gasoline constituents, including BTEX compounds, in ground water. The impact of ethanol on the size of the BTEX plume should be considered in the risk evaluation of spills of gasoline containing ethanol. FOOTPRINT was developed as a simple and user-friendly computer application that can be used as a screening model to estimate the extent of the BTEX plume when the gasoline that is spilled contains ethanol. FOOTPRINT estimates the overall area of a plume of BTEX compounds that are contained within two biodegradation zones, one zone where ethanol is present and there is no biodegradation of BTEX compounds, surrounded by a second zone where the ethanol has been removed by natural biodegradation and the rate of biodegradation of BTEX compounds is constant. Existing simple models for BTEX compounds (such as BIOSCREEN) can not model this interaction between ethanol and BTEX compounds because these models are limited to a single biodegradation rate uniformly applied across the flow path. FOOTPRINT applies a 3-dimensional analytical solute transport model to estimate solute concentration at any location downgradient from a constant concentration source for a fixed first-order decay rate. It first uses an estimate of the rate of ethanol biodegradation to estimate the zone downgradient from the source where ethanol inhibits BTEX biodegradation. Within this zone, concentrations of BTEX compounds can only attenuate through dilution and dispersion. Downgradient from this zone, FOOTPRINT models BTEX biodegradation at a constant rate. FOOTPRINT assumes that the concentration of BTEX at the source is constant. It allows either a constant concentration or exponentially decaying source for ethanol. FOOTPRINT could also be applied to estimate the plume area of any single chemical compound downgradient from a constant concentration source for a constant decay rate. Finally, results obtained from simulating FOOTPRINT for a synthetic case study were verified by comparing with the results from a conceptually identical numerical model.

## Introduction

Ethanol could be used as an oxygenate in gasoline as opposed to MTBE. A potential impact from using ethanol in gasoline is that in case of a spill, ethanol might inhibit natural attenuation of the other gasoline constituents (e.g., BTEX compounds) by depleting the electron acceptors and nutrients in the subsurface. As a result, the plumes of BTEX compounds could persist for an extended period of time. Inhibition of biodegradation of BTEX compounds along with the effect of increased solubility of the BTEX compounds and other gasoline constituents (cosolvency) due to the presence of ethanol might cause the BTEX plume to be longer than otherwise would be the case. It would be useful to have a simple approach to evaluate the potential impact of ethanol in gasoline on the size of the BTEX plume.

Deeb et al. (2002) conducted a study to estimate the effect of ethanol on the size of the benzene plume from a spill of ethanol-blended gasoline. They presented a conceptual approach to estimate the impact of ethanol on the length of the benzene plume. As long as ethanol was present in ground water above a critical concentration, natural biodegradation of benzene or any BTEX compound, was inhibited. In the presence of ethanol, the only processes that contributed to the attenuation of benzene were non-biological processes such as dispersion or sorption. When the ethanol degraded to the critical concentration, then biodegradation of benzene and the other BTEX compounds could begin.

In this study, we developed a simple computer application, named FOOTPRINT, to estimate the length of any two contaminants in ground water, when the contaminants behaved like ethanol and benzene in the approach of Deeb et al. (2002). We expanded the approach of Deeb et al. (2002) to estimate the total area of the plume, instead of the plume length. The probability that a spill will impact a receptor is more closely related to the area of a plume than to its length.

## Analytical Model for Solute Transport Through Saturated Zone

The governing equation for solute transport through a saturated soil, called the Advection-Dispersion-Equation (ADE) is derived from conservation of mass in an elementary volume of porous media. The ADE is based on the assumptions that the porous media is homogeneous and isotropic, and that the flow condition follows Darcy's law. The general form of the 3-dimensional ADE for a miscible and degradable solute in a homogeneous medium with uniform groundwater velocity in the horizontal direction (X-axis) and with equilibrium partitioning between the solid and liquid phase (equilibrium sorption) is given by:

$$R \frac{\partial C}{\partial t} = - \left( v_x \frac{\partial C}{\partial x} \right) + \left( D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \right) + \frac{W}{n} C_0 - \frac{Q}{n} C - \lambda C \quad (1)$$

where  $C$  is the solute concentration (mg/L),  $v_x$  is the average fluid velocities in the X directions, respectively (m/d), and  $D_x$ ,  $D_y$ ,  $D_z$  are the hydrodynamic dispersion coefficients in the X, Y, and Z directions (m<sup>2</sup>/d), respectively,  $n$  is the porosity of the medium (m<sup>3</sup>/m<sup>3</sup>),  $W$  and  $Q$  are volume of water injected and extracted per unit volume of aquifer per unit time (d<sup>-1</sup>), respectively,  $\lambda$  is the first order decay constant in the aqueous phase(d<sup>-1</sup>), and  $R$  is the retardation factor for sorption. For linear sorption,  $R$  is expressed as

$$R = 1 + \frac{p_b}{n} K_p \quad (2)$$

where,  $p_b$  is soil bulk density (Kg/L) and  $K_p$  is the linear sorption coefficient (L/Kg).

Domenico (1987) provided a solution of Equation (1) for a finite and constant concentration source at the top of the aquifer (see Equation 3)

$$C(x, y, z, t) = \frac{C_0}{8} \cdot f_x \cdot f_y \cdot f_z \quad (3)$$

where,  $C_0$  is the constant concentration at the source, and

$$f_x = \exp \left[ \frac{x}{2\alpha_x} \left\{ 1 - \left( 1 + \frac{4\lambda\alpha_x}{v_c} \right)^{1/2} \right\} \right] \cdot \operatorname{erfc} \left[ \left\{ x - v_c t \left( 1 + \frac{4\lambda\alpha_x}{v_c} \right)^{1/2} \right\} / 2\sqrt{\alpha_x v_c t} \right]$$

$$f_y = \left[ \operatorname{erf} \left( \frac{y + Y_S/2}{2\sqrt{D_y t}} \right) - \operatorname{erf} \left( \frac{y - Y_S/2}{2\sqrt{D_y t}} \right) \right]$$

$$f_z = \left[ \operatorname{erf} \left( \frac{z + Z_S}{2\sqrt{D_z t}} \right) - \operatorname{erf} \left( \frac{z - Z_S}{2\sqrt{D_z t}} \right) \right]$$

where,  $\alpha_x$  is the longitudinal dispersivity (m),  $v_c$  is the contaminant velocity ( $= v_x/R$ ),  $Y_S$ , and  $Z_S$  represent source dimensions along the y and z directions (m), respectively, and  $\operatorname{erf}$  and  $\operatorname{erfc}$  represent the error function and complementary error function, respectively.

Figure 1 shows the schematic of the Domenico (1987) model (Equation 3). The source in the model is assumed to be rectangular in the vertical plane and is oriented perpendicular to groundwater flow. The model is applicable in a uniform flow field with advection in the x-direction and dispersion in all three directions. Also, the source is assumed to be at the top of a semi-infinite aquifer, i.e., the aquifer is infinite in only one side of the vertical dimension. Equation 3 is used in the BIOSCREEN Natural Attenuation Decision Support System (Newell et al., 1996), which is a public domain screening tool for simulating natural attenuation of dissolved hydrocarbons at petroleum fuel release sites. BIOSCREEN was developed by Air Force Center for Environmental Excellence (AFCEE) and is distributed by the U.S. EPA's Robert S. Kerr Environmental Research Center (RSKERC).

Martin-Hayden and Robbins (1997) modified the Domenico (1987) model by using the full Ogata and Banks (1961) terms instead of the truncated version used by Domenico. Martin-Hayden and Robbins (1997) replaced the  $f_x$  term in Equation 3 with  $f'_x$ , which is given by Equation 4.

$$f'_x = \exp \left[ \frac{x}{2\alpha_x} \left\{ 1 - \left( 1 + \frac{4\lambda\alpha_x}{v_c} \right)^{1/2} \right\} \right] \cdot \operatorname{erfc} \left[ \left\{ x - v_c t \left( 1 + \frac{4\lambda\alpha_x}{v_c} \right)^{1/2} \right\} / 2\sqrt{\alpha_x v_c t} \right] \\ + \exp \left[ \frac{x}{2\alpha_x} \left\{ 1 + \left( 1 + \frac{4\lambda\alpha_x}{v_c} \right)^{1/2} \right\} \right] \cdot \operatorname{erfc} \left[ \left\{ x + v_c t \left( 1 + \frac{4\lambda\alpha_x}{v_c} \right)^{1/2} \right\} / 2\sqrt{\alpha_x v_c t} \right] \quad (4)$$

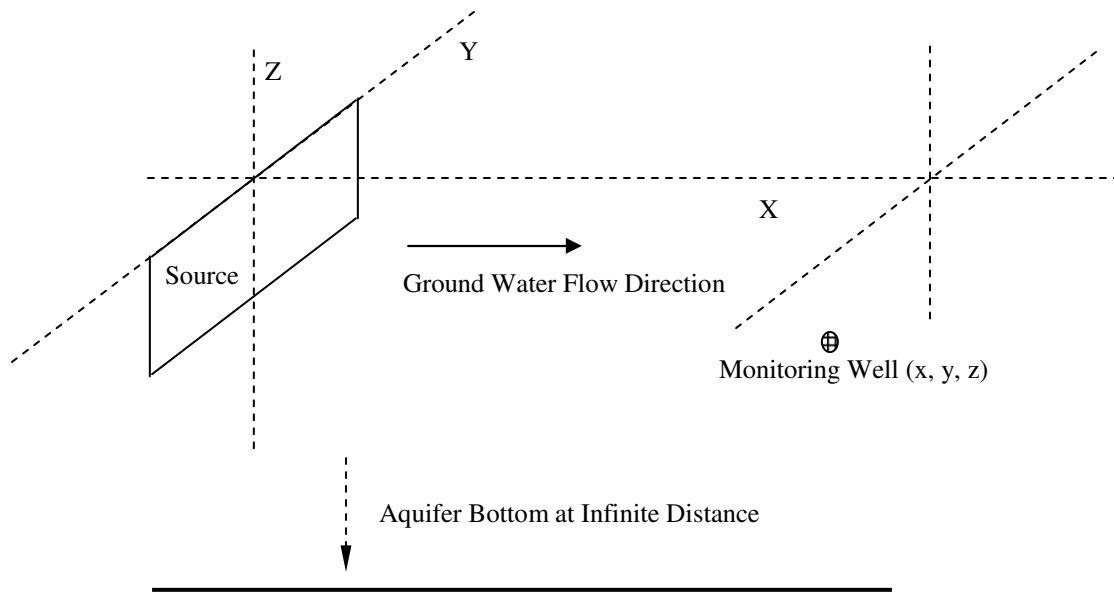


Figure 1. Schematic of Domenico model used in BIOSCREEN

Equation 4 is used in the BIOCHLOR Natural Attenuation Model (Aziz et al., 1999). BIOCHLOR simulates natural attenuation of chlorinated solvents subjected to sequential chain reactions, where the parent solvent biodegrades to a daughter product and that daughter biodegrades to another daughter product, and so on. BIOCHLOR was developed in collaboration with the AFCEE and RSKERC and is also distributed by the RSKERC.



## Conceptual Model Used in FOOTPRINT

The model for predicting the plume area of any gasoline constituents or other chemicals of concern (COC) as a result of accidental spill of ethanol-blended gasoline is conceptualized in FOOTPRINT according to Figure 2. Following a spill, ethanol and the gasoline constituents (or the COCs) reach the water table. Ethanol transports through the groundwater by advection and dispersion and biodegrades downgradient from the source. Biodegradation of the gasoline constituents (or the COCs) is negligible from the source to the distance where the ethanol concentration drops to a threshold concentration, i.e., no biodegradation for the COC within the distance  $L_e$  from the source (see Figure 2). According to Deeb et al. (2002), this threshold concentration of ethanol is approximately 3 mg/L for benzene. At the zone between the source and the location where the ethanol concentration reaches the threshold limit (i.e., within  $L_e$ ), the decrease in COC concentration is only due to advection, dispersion and sorption. Biodegradation of the gasoline constituent (or the COC) starts downgradient from the zone where the ethanol concentration is over the threshold concentration. First order decay is assumed for both ethanol and the COC.

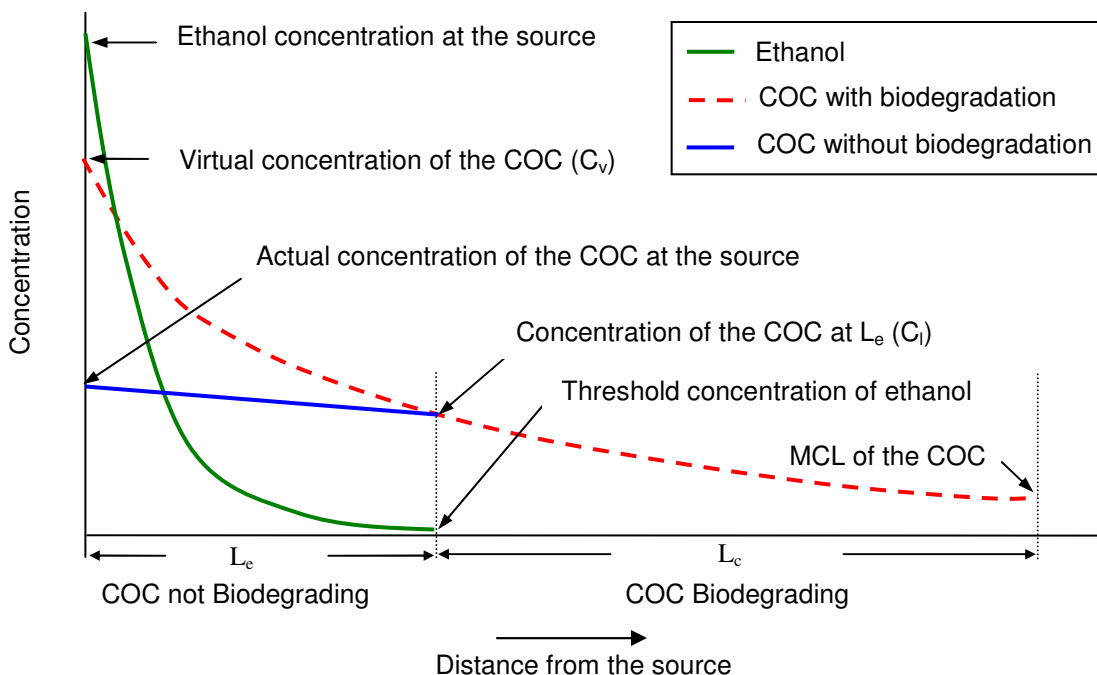


Figure 2. Conceptual model for FOOTPRINT

## Methodologies to Estimate Plume Area

### Methodology Used in FOOTPRINT

FOOTPRINT uses Equation 4, which is the modified version of the Domenico (1987) model by Martin-Hayden and Robbins (1997), to estimate solute concentration at any downgradient location from the source. However, Equation 4 could not be applied directly to the COC for the condition explained in the conceptual model shown in Figure 2. Equation 4 is limited to only one biodegradation rate, while the COC has two biodegradation zones: no decay from the source to where the ethanol concentration drops to the threshold concentration (i.e.,  $L_e$ ), and at any given decay rate downgradient from  $L_e$ . Therefore, a modified approach has been taken to apply Equation 4 to obtain the COC concentration downgradient from the source. Following are the steps of the modified approach taken in FOOTPRINT:

1. Simulate Equation 4 for ethanol at steady-state conditions (i.e., for a large time period,  $t$ ) to compute the distance  $L_e$  (see Figure 2), which is the distance along the centerline of the plume and at zero vertical distance from the water table.
2. Simulate Equation 4 for the COC with zero decay rate to compute the steady-state concentration at  $L_e$ , which is  $C_1$  in Figure 2.
3. Simulate the Inverse of Equation 4 to compute the concentration of the COC at the source ( $C_v$ ) from  $C_1$  for the given decay rate for the COC (see Figure 2).  $C_v$  is named as the virtual concentration of the COC at the source.
4. Finally, simulate Equation 4 with the virtual concentration of the COC at the source ( $C_v$ ) to compute the distance  $L_c$  (see Figure 2), where the steady-state concentration of the COC drops to the maximum contaminant level (MCL).

To calculate the area of the plume, the domain downgradient of the source is divided into a finite number of cells. Concentrations of the COC at each cell within each zone (i.e.,  $L_e$  and  $L_c$ ) are calculated from the model. The number of cells exceeding the MCL within both zones are counted and used to calculate the total plume area. Note that the area is computed for the plume at the water table, as the plume concentration should be higher in the water table compared to any other underneath horizontal planes.

### Alternative Approach

An alternative approach to the methodology outlined in the above section could also be considered. Following the first two steps stated in the above section, the third step could be skipped and the fourth steps could be applied to compute  $L_c$  for the source concentration  $C_1$  at  $L_e$ . This approach follows the assumption that the constant concentration source would shift to  $L_e$ . This assumption could be reasonable for estimating the plume length, as the simulation is conducted at steady-state condition. It seems that Deeb et al. (2002) have followed this approach to estimate the plume length for benzene from a spill of ethanol-blended gasoline. However, this approach could not be applied in estimating the plume area, as the source dimensions at  $L_e$  would be expanded from the actual source area due to dispersion.

Therefore, an underestimation of the plume area could result from this approach. A comparison between the two approaches for a given set of input values is presented in the following section.

## Verification of the Conceptual Model Used in FOOTPRINT

In order to verify the conceptual model used in FOOTPRINT, a numerical model with boundary conditions and assumptions comparable to the Domenico model was prepared. Visual MODFLOW (WHI, 1999), a Windows-based pre- and post-processing interface for groundwater flow and transport models, was used for setting up the numerical model. MODFLOW (McDonald and Harbaugh, 1988) is a 3-dimensional finite difference model for groundwater flow, developed by the U.S. Geological Survey. MT3DMS (Zheng and Wang, 1999) is a 3-dimensional multi-species numerical transport model that considers advection, dispersion, and sorption. MT3DMS (Zheng and Wang, 1999) was used for modeling transport of ethanol and the COC.

### *Numerical Model Setup*

A 600×300×30 m model domain, encompassing about 10 times the source width and depth, was considered. The model domain is set up so that the plumes never transport out of the domain and the transverse and vertical boundaries do not affect the plume. This is necessary as the Domenico model assumes infinite boundaries in the lateral and vertical directions. Constant heads at the upgradient and downgradient boundaries, and no-flow boundaries at the bottom and at the lateral sides of the model domain were selected for the flow model. Boundaries were set up to ensure a unidirectional flow field, as assumed in the Domenico model.

A 3×3×1.5 m grid dimension was used in the model. In order to verify the flow model, distance traveled by a water particle for a given time was predicted by using the particle tracking code, MODPATH (Pollock, 1994) and then compared with the same obtained from the seepage velocity. Equation 5 was used to estimate the seepage velocity ( $V_s$ ).

$$V_s = \frac{K_s \times I_g}{n \times R} \quad (5)$$

where,  $K_s$  is the saturated hydraulic conductivity (m/d),  $I_g$  is the hydraulic gradient (m/m),  $n$  is the porosity ( $m^3/m^3$ ), and  $R$  is the retardation factor.

Table 1 presents the values of all input parameters used in the model. The hydraulic conductivity value represents a loamy sand according to Carsel and Parrish (1988). Decay rates for ethanol and the COC (here, benzene), the threshold concentration limit for ethanol, and source concentrations for ethanol and benzene were obtained from Deeb et al. (2002). All other input parameters are typical values for the scale of the model. As the purpose of simulating the model is to compare the results of the numerical model with that of

FOOTPRINT and thus verify the latter, use of typical values is reasonable. Note that although Deeb et al. (2002) used 1 µg/L as the maximum contaminant level (MCL) for benzene (the primary MCL for benzene in California), a higher value for the same was assumed in this study in order to minimize the computational time required for simulating the numerical model.

### *Numerical Model Simulation and Comparison of Modeling Results*

The numerical transport model (i.e., MT3DMS) was first simulated for ethanol. An iso-concentration map for the ethanol plume, outlined by the threshold limit (e.g., 3 mg/L), was plotted. Then, the decay rate for the COC was set to zero within the zone where the ethanol concentration is over 3 mg/L, while the decay rate away from that zone was set to the given value (see Table 1). Simulations of the transport model for both the COC and ethanol were conducted for a long time (about 15,000 days) so that the downgradient concentration reaches steady state. Note that the ‘no biodegradation zone’ for the COC ( $L_e$ ) remains fixed in size due to the assumptions of constant ethanol source concentration and a steady state condition. For a decaying ethanol source, the ‘no biodegradation zone’ would shrink with time.

Table 1. Input parameters used for model verification.

| Parameters   | Values |
|--|--------|
| Hydraulic conductivities in X and Y directions (m/d) | 3.3    |
| Hydraulic conductivities in Z direction (m/d)        | 0.33   |
| Hydraulic gradient (m/m)                             | 0.005  |
| Effective porosity ( $m^3/m^3$ )                     | 0.20   |
| Longitudinal dispersivity (m)                        | 12     |
| Transverse dispersivity (m)                          | 1.2    |
| Vertical dispersivity (m)                            | 0.0012 |
| Source width (m)                                     | 30     |
| Source thickness (m)                                 | 3.0    |
| Ethanol/Oxygenate concentration at the source (mg/L) | 4000   |
| Decay rate for ethanol (1/year)                      | 5.11   |
| Threshold concentration of ethanol (mg/L)            | 3.0    |
| COC concentration at the source (mg/L)               | 8      |
| COC maximum contamination level (mg/L)               | 0.08   |
| Decay rate for COC (1/year)                          | 2.26   |
| Retardation Factors for both ethanol and COC         | 1.0    |

Simulation results obtained from the numerical model (i.e., Visual MODFLOW), FOOTPRINT and the alternative technique discussed earlier are presented in Table 2. It is observed that all three techniques resulted in equivalent values for the plume length (i.e.,  $L_e + L_c$ ). Also, the plume area estimation from the technique used in FOOTPRINT results in a less than 4% error for the given input values (Table 1) when compared to the results from the numerical model. However, the alternative technique produced about 42% error in estimating the plume area. This discrepancy in the plume area estimation by the alternative technique resulted from underestimation of lateral spreading of the plume. Even larger error could

result for a dispersion dominated transport condition. On the contrary, less error is likely for advection dominated transport.

Table 2. Comparison of modeling results for constant concentration sources.

| Parameters                          | Numerical Model | FOOTPRINT | Error (%) | Alternative Technique | Error (%) |
|-------------------------------------|-----------------|-----------|-----------|-----------------------|-----------|
| L <sub>e</sub> (m)                  | 78.3            | 78.0      | -0.38     | 78.0                  | -0.38     |
| L <sub>c</sub> (m)                  | 80.5            | 80.2      | -0.37     | 79.0                  | -1.86     |
| L <sub>e</sub> + L <sub>c</sub> (m) | 155.0           | 158.2     | 2.06      | 157.0                 | 1.29      |
| Plume Area (m <sup>2</sup> )        | 10,740          | 11,130    | 3.63      | 6,200                 | -42.3     |

## Decaying Ethanol Source

Analytical model for an exponentially decaying source is presented in BIOCHLOR version 2.2, which is available from the RSKERC web page (<http://www.epa.gov/ada/csmos.html>). The model is an extension of the original Domenico (1987) model. Equation 6 presents the model for an exponentially decaying source, i.e., at the source,  $C = C_0 \exp(-k_s t)$ , where  $C_0$  is the initial concentration at the source and  $k_s$  is the first order decay rate.

$$C(x, y, z, t) = \frac{C_0}{8} e^{-k_s t} \cdot f_x'' \cdot f_y \cdot f_z \quad (6)$$

where,  $f_y$  and  $f_z$  are same as Equation 3, and

$$f_x'' = \exp \left[ \frac{x}{2\alpha_x} \left\{ 1 - \left( 1 + \frac{4(\lambda - k_s)\alpha_x}{v_c} \right)^{1/2} \right\} \right] \cdot \operatorname{erfc} \left[ \left\{ x - v_c t \left( 1 + \frac{4(\lambda - k_s)\alpha_x}{v_c} \right)^{1/2} \right\} / 2\sqrt{\alpha_x v_c t} \right] \\ + \exp \left[ \frac{x}{2\alpha_x} \left\{ 1 + \left( 1 + \frac{4(\lambda - k_s)\alpha_x}{v_c} \right)^{1/2} \right\} \right] \cdot \operatorname{erfc} \left[ \left\{ x + v_c t \left( 1 + \frac{4(\lambda - k_s)\alpha_x}{v_c} \right)^{1/2} \right\} / 2\sqrt{\alpha_x v_c t} \right]$$

where,

$$k_s \leq \left[ \frac{4\alpha_x \lambda + v_c}{4\alpha_x} \right] \quad (7)$$

FOOTPRINT uses Equation 6 for a decaying ethanol source. The simulation procedure for a decaying ethanol source remains the same as the constant ethanol source, except that the modeling condition is transient rather than steady state. Since the ethanol concentration at the source is changing with time for a decaying source, the downgradient concentration can not

reach steady state. Therefore, the ‘no biodegradation zone’ for the COC would change with time, and plume area of the COC would change as well. FOOTPRINT conducts the simulation for a decaying ethanol source in increasing time steps and computes the COC plume area at every time step. Therefore, the output from FOOTPRINT shows the change in COC plume area with time instead of a fixed plume area as obtained for a constant ethanol source.

## Notice

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## Appendix B : Analytical Model for Zero-Order Decay

### Analytical Solution for Zero-Order Decay in the Plume

The Advection-Dispersion-Equation (ADE) for zero-order decay in the plume is given by:

$$R \frac{\partial C}{\partial t} = - \left( v_x \frac{\partial C}{\partial x} \right) + \left( D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \right) - \gamma \quad (1)$$

where  $C$  is the solute concentration (mg/L),  $v_x$  is the average seepage velocities in the  $X$  directions, respectively (m/d), and  $D_x$ ,  $D_y$ ,  $D_z$  are the hydrodynamic dispersion coefficients in the  $X$ ,  $Y$ , and  $Z$  directions (m<sup>2</sup>/d), respectively,  $\gamma$  is the zero-order decay constant in the aqueous phase (mg/L/d<sup>-1</sup>), and  $R$  is the retardation factor for sorption. For linear sorption,  $R$  is expressed as

$$R = 1 + \frac{p_b}{n} K_p \quad (2)$$

where,  $p_b$  is soil bulk density (Kg/L) and  $K_p$  is the linear sorption coefficient (L/Kg).

Solution of Equation (1) for the following boundary and initial conditions (Equations 3 to 5) is shown in Equation 6.

$$C(0, t) = C_0 \text{ (i.e., constant source concentration at the top of the aquifer)} \quad (3)$$

$$C(x, 0) = 0 \text{ (i.e., zero initial concentration down gradient from the source)} \quad (4)$$

$$\frac{\partial C}{\partial x}(\infty, t) = 0 \quad (5)$$

$$C(x, y, z, t) = \frac{1}{4} \cdot f_x^0 \cdot f_y \cdot f_z \quad (6)$$

where,  $f_x^0$  is obtained from modifying the solution provided by van Genuchten (1981) (pp. 231), which assumes one-dimensional ADE with zero-order growth in the plume.

$$f_x^0 = C_0 A(x, t) - B(x, t); \text{ where, } A(x, t) = \frac{1}{2} \exp\left(\frac{x}{\alpha_x}\right) \cdot \operatorname{erfc}\left[\frac{(x + v_c t)}{2\sqrt{\alpha_x v_c t}}\right] + \frac{1}{2} \operatorname{erfc}\left[\frac{(x - v_c t)}{2\sqrt{\alpha_x v_c t}}\right] \quad (7)$$

$$B(x, t) = \frac{\gamma}{R} \left\{ t - \frac{(x + v_c t)}{2v_c} \exp\left(\frac{x}{\alpha_x}\right) \cdot \operatorname{erfc}\left[\frac{(x + v_c t)}{2\sqrt{\alpha_x v_c t}}\right] + \frac{(x - v_c t)}{2v_c} \operatorname{erfc}\left[\frac{(x - v_c t)}{2\sqrt{\alpha_x v_c t}}\right] \right\} \quad (8)$$



$$f_y = \left[ \operatorname{erf} \left( \frac{y + Y_S/2}{2\sqrt{D_y t}} \right) - \operatorname{erf} \left( \frac{y - Y_S/2}{2\sqrt{D_y t}} \right) \right] \quad (9)$$

$$\text{And } f_z = \left[ \operatorname{erf} \left( \frac{z + Z_S}{2\sqrt{D_z t}} \right) - \operatorname{erf} \left( \frac{z - Z_S}{2\sqrt{D_z t}} \right) \right] \quad (10)$$

where,  $\alpha_x$  is the longitudinal dispersivity (m),  $v_c$  is the contaminant velocity ( $= v_x/R$ ),  $Y_S$ , and  $Z_S$  represent source dimensions along the y and z directions (m), respectively, and *erf* and *erfc* represent the error function and complementary error function, respectively.

## Exponentially Decaying Source with Zero-Order decay in the Plume

The analytical model for a constant concentration source (Equations 6-10) can be modified to represent a source concentration that is decaying exponentially. Equation 11 presents the model for an exponentially decaying source, i.e., at the source,  $C = C_0 \exp(-k_s t)$ , where  $C_0$  is the initial concentration at the source and  $k_s$  is the first-order decay rate.

$$C(x, y, z, t) = \frac{1}{4} \cdot f_{xd}^0 \cdot f_y \cdot f_z \quad (11)$$

where,  $f_{xd}^0$  is obtained from modifying the solution provided by van Genuchten (1981) (pp. 231), which assumes one-dimensional ADE with exponentially decaying source and zero-order growth in the plume.

$$f_{xd}^0 = C_0 D(x, t) - B(x, t);$$

where,

$$D(x, t) = \exp(-k_s t) \left\{ \frac{1}{2} \exp \left[ \frac{(v_c - \xi)x}{2\alpha_x v_c} \right] \cdot \operatorname{erfc} \left[ \frac{(x - \xi t)}{2\sqrt{\alpha_x v_c t}} \right] + \frac{1}{2} \exp \left[ \frac{(v_c + \xi)x}{2\alpha_x v_c} \right] \cdot \operatorname{erfc} \left[ \frac{(x + \xi t)}{2\sqrt{\alpha_x v_c t}} \right] \right\} \quad (12)$$

$$\text{and, } \xi = v_c \left[ 1 - \frac{4k_s \alpha_x}{v_c} \right]^{1/2} \quad (13)$$

It should be noted that for any exponentially decaying source, the decay rate ( $k_s$ ) should be limited to the following equation,

$$k_s \leq \left[ \frac{v_c}{4\alpha_x} \right] \quad (14)$$

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## Appendix C: Expression for Zero-Order Decay in both Aqueous and Solid Phases

### Expression for Zero-Order Decay in both Aqueous and Solid Phases

The Advection-Dispersion-Equation (ADE) for zero-order decay occurring **in both aqueous and solid phases** in the plume is given by:

$$\frac{\partial}{\partial t}(\theta C + \rho_b S) = -\left(q \frac{\partial C}{\partial x}\right) + \left(\theta(D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2})\right) - \theta \gamma_L - \rho_b K_p \gamma_s \quad (1)$$

$$R \frac{\partial C}{\partial t} = -\left(v_x \frac{\partial C}{\partial x}\right) + \left(D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2}\right) - \gamma_L - \frac{\rho_b}{\theta} K_p \gamma_s \quad (2)$$

$$R \frac{\partial C}{\partial t} = -\left(v_x \frac{\partial C}{\partial x}\right) + \left(D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2}\right) - \gamma \quad (3)$$

where,  $C$  is the solute concentration (mg/L);  $v_x$  is the average seepage velocity in the  $X$  direction (m/d);  $D_x$ ,  $D_y$ ,  $D_z$  are the hydrodynamic dispersion coefficients in the  $X$ ,  $Y$ , and  $Z$  directions ( $m^2/d$ ), respectively;  $\gamma_L$  and  $\gamma_s$  are the zero-order decay constants in the aqueous and solid phases (mg/L/d), respectively;  $R$  is the retardation factor for sorption;  $\rho_b$  is soil bulk density (Kg/L);  $\theta$  is volumetric moisture content ( $L^0$ ), which is equal to soil porosity ( $n$ ) at saturated condition;  $K_p$  is the linear sorption coefficient ( $m^3/Kg$ ) and  $\gamma$  is lumped zero-order decay constant for both aqueous and solid phases (mg/L/d). Note that the zero order decay rates are in term of decay in the aqueous concentration per day.

$R$  is expressed as:

$$R = 1 + \frac{\rho_b}{n} K_p \quad (4)$$

where,  $K_p$  is the linear sorption coefficient (L/Kg),

The lumped zero-order decay constant  $\gamma$  is given as follows:

$$\begin{aligned}\gamma &= \gamma_L + \frac{\rho_b}{n} K_p \gamma_s \\ &= \gamma_L \left(1 + \frac{\rho_b}{n} K_p \frac{\gamma_s}{\gamma_L}\right)\end{aligned}\tag{5}$$

When,  $\gamma_L = \gamma_s$

Then,

$$\begin{aligned}\gamma &= \gamma_L \left(1 + \frac{\rho_b}{n} K_p\right) \\ &= \gamma_L R\end{aligned}\tag{6}$$

## Appendix D: Expression for First-Order Decay in both Aqueous and Solid Phases

### Expression for First-Order Decay in both Aqueous and Solid Phases

The Advection-Dispersion-Equation (ADE) for first-order decay occurring **in both aqueous and solid phases** in the plume is given by:

$$\frac{\partial}{\partial t}(\theta C + \rho_b S) = -\left(q \frac{\partial C}{\partial x}\right) + \left(\theta(D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2})\right) - \lambda_L \theta C - \lambda_s \rho_b S \quad (1)$$

$$R \frac{\partial C}{\partial t} = -\left(v_x \frac{\partial C}{\partial x}\right) + \left(D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2}\right) - (\lambda_L + \lambda_s \frac{\rho_b}{\theta} K_p) C \quad (2)$$

$$R \frac{\partial C}{\partial t} = -\left(v_x \frac{\partial C}{\partial x}\right) + \left(D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2}\right) - \lambda C \quad (3)$$

where,  $C$  is the solute concentration (mg/L),  $v_x$  is the average seepage velocity in the  $X$  direction (m/d);  $D_x$ ,  $D_y$ ,  $D_z$  are the hydrodynamic dispersion coefficients in the  $X$ ,  $Y$ , and  $Z$  directions ( $m^2/d$ ), respectively;  $\lambda_L$  and  $\lambda_s$  are the first-order decay constants in the aqueous and solid phases (1/d), respectively;  $R$  is the retardation factor for sorption;  $\rho_b$  is soil bulk density (Kg/L);  $\theta$  is volumetric moisture content ( $L^3/L^3$ ), which is equal to soil porosity ( $n$ ) at saturated condition;  $\lambda$  is lumped first-order decay constant in aqueous and solid phases (1/d).

$R$  is expressed as:

$$R = 1 + \frac{\rho_b}{n} K_p \quad (4)$$

where,  $K_p$  is the linear sorption coefficient (L/Kg).

The lumped first-order decay constant  $\lambda$  is given as:

$$\begin{aligned} \lambda &= (\lambda_L + \lambda_s \frac{\rho_b}{n} K_p) \\ &= \lambda_L (1 + \frac{\rho_b}{n} K_p \frac{\lambda_s}{\lambda_L}) \end{aligned} \quad (5)$$

If  $\lambda_L = \lambda_s$  Then

$$\lambda = \lambda_L R \quad (6)$$